* NOTICES *

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2.**** shows the word which can not be translated.
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CLAIMS

(57) [Claim(s)]
[Claim 1](a) A polymer whose substantial repeating unit it has a reactive silicon group and is -$CH_2CH_2CH_2CH_2O$-, (b) A bisphenol A type epoxy resin, a silane coupling agent which contains an amino group and alkoxy silyl groups in one molecule (c), (d) A hardenability resin composite which consists of an epoxy resin hardener which is a silanol condensation catalyst which is a tin compound containing tetravalent tin and the (e) third class amine compound, or its salt.
[Claim 2](a) The hardenability resin composite according to claim 1, wherein a main chain of a polymer of an ingredient is polyether obtained from a tetrahydrofuran by ring opening polymerization, or polyether obtained from a tetrahydrofuran and cyclic ether by ring opening polymerization.
[Claim 3](b) The hardenability resin composite according to claim 1 or 2, wherein an ingredient is an epichlorohydrin bisphenol A type epoxy resin obtained from bisphenol A and epichlorohydrin.
[Claim 4](c) A hardenability resin composite given in any 1 clause of Claims 1-3 to which a blending ratio of a silane coupling agent of an ingredient is characterized by being 0.01 - 50 weight section to (a) ingredient 100 weight section.
[Claim 5](d) A hardenability resin composite given in any 1 clause of Claims 1-4 to which a blending ratio of a silanol condensation catalyst of an ingredient is characterized by being 0.01 - 20 weight section to (a) ingredient 100 weight section.
[Claim 6](e) A hardenability resin composite given in any 1 clause of Claims 1-5 to which a blending ratio of an epoxy resin hardener of an ingredient is characterized by being 0.01 - 300 weight section to (b) ingredient 100 weight section.
[Claim 7]A control method of phase structure of a hardened material facing controlling phase structure of a hardened material produced by making harden the hardenability resin composite according to claim 1, and changing an addition of a silane coupling agent.
[Claim 8](c) A method of carrying out 0.01-50 weight-section addition of the silane coupling agent of an ingredient to polymer 100 weight section of the (a) ingredient according to claim 7.

[Translation done.]

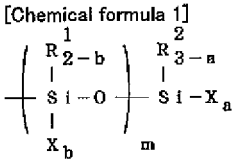
* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]This invention relates to a hardenability resin composite. It is related with the hardenability resin composite excellent in the adhesive property by which the phase separation structure produced in more detail in the process to harden was controlled.
[0002]
[Description of the Prior Art]Since the polymer which has a reactive silicon group (basis which is a silicon atom content group containing the silicon atom which the hydroxyl group or the hydrolytic basis combined, and can form a siloxane bond) carries out bridge construction hardening under moisture existence, it can use as a hardenability resin composite. Generally that in which the principal chain skeleton is polyether in these polymer is known as modified silicone, and is widely used for the sealing agent etc.
[0003]It dissolves with the polymer which has a reactive silicon group, and by hardening, phase separation of the mixture with the hardening resin hardened by a different hardening reaction from this can be carried out, and it can turn into a hardened material in which various phase structure is shown. As such a mixture, there is a constituent with the polymer which has a reactive silicon group, this, the dissolving phenol resin, or an epoxy resin. The hardened material obtained from these constituents becomes the thing excellent in intensity or toughness as compared with what stiffened each resin independently. These constituents can be stored under sealing and it is suitably used as 2 liquid system adhesives in which moderate elasticity is shown (JP,61-83220,A, JP,61-247723,A, JP,62-84134,A, JP,63-3012,A). The phase structure of the hardened material obtained from the constituent of the polypropylene oxide which has a reactive silicon group, and a bisphenol A type epoxy resin in these, Usually, the polypropylene oxide which has the hardened reactive silicon group is made into a matrix, and the hardened epoxy resin has structure (domain structure of a ball/matrix) distributed in the domain of 0.05-0.5 micrometer in diameter particle state. Although this hardened material shows high elongation after fracture and high breaking strength, it is thought that this is based on the reinforcing effect of the epoxy resin hardened to particle state (the Society of Polymer Science, Japan proceedings, 36 No. 2, 394 pages).
[0004]
[Problem to be solved by the invention]In the hardened material obtained from the constituent which consists of the polymer and this which have a reactive silicon group, and a dissolving epoxy resin, the cohesive force of a matrix influences the physical properties of a hardened material greatly. Since the cohesive force is small when the polypropylene oxide which has a reactive silicon group serves as a matrix, still bigger bond strength, especially tensile shear strength may be needed. In order to raise intensity and toughness further by the curing system which consists of this constituent, while lowering the particle diameter of an epoxy resin and heightening a reinforcing effect, what the amount of epoxy resins in a matrix is made to increase, and the cohesive force of a matrix is raised for (the phase structure of a hardened material is controlled) can be considered.
[0005]However, generally in the curing system acquired from the constituent of the polypropylene oxide which has a reactive silicon group, and an epoxy resin, phase structure control of a hardened material is difficult. It cannot be considered as the above phase structure considered to raise physical properties, such as an elastic modulus and tensile shear strength, further, and to get by addition of change of the composition ratio of a constituent, a silane coupling agent, etc. although a certain amount of control is possible.
[0006]This invention is made in view of the above-mentioned fact, and is a thing.
The purpose is to provide the hardenability resin composite which can control the phase structure of **, to

which the particle diameter of a distributed epoxy resin particle and the intensity of a matrix can be changed substantially and in which especially an elastic modulus and tensile shear strength have been improved.

[0007]
[Means for solving problem]The phase structure of a hardened material obtained from a constituent which consists of a polymer and this which have a reactive silicon group, and a dissolving epoxy resin can consider being influenced by addition etc. of both compatibility, a cure rate, and a specific compound that can react with both, i.e., a silane coupling agent.
[0008]Inventors found out that a thing containing repeating unit-$CH_2CH_2CH_2CH_2O$- was excellent in especially compatibility with an epoxy resin in a polymer which has a reactive silicon group. In a constituent which blended this polymer, a dissolving epoxy resin, a condensation catalyst, an epoxy resin hardener, and a silane coupling agent, Phase structure of a hardened material changed especially with addition of a silane coupling agent substantially, while particle diameter of an epoxy resin particle distributed in a hardened material fell, the amount of epoxy resins in a matrix increased, and it found out becoming a hardened material of high tension shear strength at a rate of high elasticity, and resulted in this invention.
[0009]Namely, a hardenability resin composite of this invention has the (a) reactive silicon group, A polymer whose substantial repeating unit is $-CH_2CH_2CH_2CH_2O-$, (b) It consists of an epoxy resin hardener which is a bisphenol A type epoxy resin, a silane coupling agent which contains an amino group and alkoxy silyl groups in one molecule (c), a silanol condensation catalyst which is the tin compounds containing tin of (d) tetravalence and the (e) third class amine compound, or its salt.
[0010]Especially in this hardenability resin composite, phase structure of a hardened material can be controlled by a kind and an addition of a silane coupling agent, and cohesive force of a matrix can be changed. As a result, a hardened material of high tension shear strength can also be obtained at a rate of high elasticity which raised cohesive force of not only a hardened material of high elongation but a matrix with the conventional low elastic modulus.
[0011]Although a principal chain skeleton of a polymer of the (a) ingredient contained in this invention is generally obtained by ring opening polymerization of a tetrahydrofuran, A tetrahydrofuran, and ethyleneoxide, propylene oxide, Copolymerization of the acid anhydrides, such as lactone, such as cyclic ether, such as alkylene oxide like allyl glycidyl ether, oxetane, and oxepane, beta propiolactone, delta-valerolactone, and epsilon-caprolactone, a succinic anhydride, and phthalic anhydride, may be carried out. Two or more sorts of these copolymerizable monomers may be used together. A polymer obtained from a tetrahydrofuran and a copolymerizable monomer may be a random copolymer, a block copolymer, a graft copolymer, or an alternating copolymer, and may be such mixed structures. It may be a mixture of a polymer in which such structures differ.
[0012](a) Although a reactive silicon group in particular contained in an ingredient is not limited, if a typical thing is shown, a following general formula and a basis expressed with ** 1 will be mentioned, for example.
[0013]
[Chemical formula 1]



R^1 and R^2 among [type, All An alkyl group of the carbon numbers 1-20, an aryl group of the carbon numbers 6-20, When the Tori ORGANO siloxy group shown by an aralkyl group of the carbon numbers 7-20 or $(R')_3SiO-$ is shown and R^1 or two or more R^2 exist, they may be the same and may differ. R' is a univalent hydrocarbon group of the carbon numbers 1-20 here, and three R' may be the same and may differ. X shows a hydroxyl group or a hydrolytic basis, and when two or more X exists, they may be the same and may differ. As for a, 0, 1, 2, or 3b shows 0, 1, or 2, respectively. m pieces [0014]
[Chemical formula 2]

b which can be boiled and set may differ. m shows the integer of 0-19. However, a+sigma b>=1 shall be satisfied. The hydrolytic basis in particular shown by the] above X is not limited, but should just be a conventionally publicly known hydrolytic basis. Specifically, a hydrogen atom, a halogen atom, an alkoxy group, an acyloxy group, a KETOKISHI mate group, an amino group, an amide group, an acid-amide group, an aminooxy group, a sulfhydryl group, an alkenyloxy group, etc. are mentioned, for example. Among these, although a hydrogen atom, an alkoxy group, an acyloxy group, a KETOKISHI mate group, an amino group, an amide group, an aminooxy group, a sulfhydryl group, and an alkenyloxy group are preferred, the viewpoint of hydrolysis nature being quiet and being easy to deal with it to especially an alkoxy group is preferred.

[0015]1-3 of of this hydrolytic basis and hydroxyl group can be combined with one silicon atom, and, as for (a+sigmab), it is preferred that it is 1-5. When a hydrolytic basis and a hydroxyl group combine with the two or more same silicon atoms, they may be the same and may differ.

[0016]Although there may be one silicon atom and there may be two or more pieces in a reactive silicon group, in the case of a reactive silicon group with which a silicon atom was connected by siloxane bond etc., there may be about 20 pieces.

[0017]a reactive silicon group expressed with a following general formula and ** 3 — acquisition — from an easy point, it is desirable.

[0018]

[Chemical formula 3]

(R^2, X, and a are the same as the above among a formula.) Again as an example of R^1 in the above-mentioned general formula and ** 1, and R^2, For example, cycloalkyl groups, such as alkyl groups, such as a methyl group and an ethyl group, and a cyclohexyl group, Aralkyl groups, such as aryl groups, such as a phenyl group, and benzyl, the Tori ORGANO siloxy group R' is indicated to be by $_3SiO-$ which is a methyl group, a phenyl group, etc. (R'), etc. are mentioned. Especially as R^1, R^2, and R', a methyl group is preferred.

[0019]A reactive silicon group is good for 1.1-5 pieces to exist preferably in [at least one] one molecule of polymers. Since hardenability becomes insufficient, and the network structure will become too much dense if too large, it stops showing a good mechanical characteristic, if the number of reactive silicon groups contained in one molecule of polymers will be less than one piece.

[0020]A reactive silicon group may exist in the end of a polymer chain, and may exist in an inside, or may exist in both. Since the effective network chain density of the polymer component contained in the hardened material formed eventually increases when a reactive silicon group exists in the end of a chain especially, it is desirable from points, like the hardened material excellent in the mechanical property becomes is easy to be obtained.

[0021](a) An ingredient may be straight chain shape, or it may have branching and the molecular weight is 1,000-20,000 more preferably 500 to about 50,000.

[0022]As an example of an ingredient, (a) JP,45-36319,B, JP,46-12154,B, JP,50-156599,A, JP,54-6096,A, JP,55-13767,A, Although what is indicated by gazettes, such as JP,55-13468,A, JP,55-137129,A, JP,57-164123,A, and JP,3-2450,B, is raised and these are used effectively, it is not limited to in particular these.

[0023]As an epoxy resin of the (b) ingredient contained in this invention, Epichlorohydrin bisphenol A type epoxy resin;. Epichlorohydrin bisphenol-F-type-epoxy-resin;. Epichlorohydrin bisphenol smooth S form epoxy resin;. fire retardancy type epoxy resin [, such as glycidyl ether of tetrabromobisphenol A,]; — novolak-type-epoxy-resin; — hydrogenation bisphenol A type epoxy resin; — the glycidyl ether type epoxy resin of a bisphenol A type propylene oxide addition. Glycidyl ether type epoxy resins, such as a bisphenol A type ethylene oxide addition; Diglycidyl p-oxybenzoic acid, Phthalic acid diglycidyl ester, tetrahydrophtal

acid diglycidyl ester, Glycidyl ester typed epoxy resin, such as diglycidyl hexahydrophthalate and adipic acid diglycidyl ester; Triglycidyl m-aminophenol, N,N,N', and N'-tetraglycidyl ether diaminodiphenylmethane, N, and N-diglycidyl aniline, glycidyl amine-type-epoxy-resin [, such as N,N-diglycidyl o-toluidine,]; — hydantoin type epoxy resin [, such as 1,3-diglycidyl 5-methyl-5-ethylhydantoin,]; — triglycidyl isocyanurate; — polyalkylene glycol diglycidyl ether;. Glycerin, glycidyl ether of polyhydric alcohol like sorbitol; An ant cyclic diepoxy acetal, Cyclic aliphatic series epoxy resins, such as ant cyclic diepoxy AJIPETO, ant cyclic diepoxy carboxylate, and vinyl cyclohexane oxide; although the epoxidation thing of an unsaturation polymer, etc. are illustrated at the time, such as polybutadiene and petroleum resin, Not the thing limited to these but the epoxy resin currently generally used can be used. What contains two or more epoxy groups among these epoxy resins tends to form the network structure, and is preferred. The point of compatibility with the (a) ingredient to the epoxy resin which has glycidyl ether more preferably, especially an epichlorohydrin bisphenol A type epoxy resin are preferred.

[0024](b) as for the addition of an ingredient, 5-900 copies are preferred to 100 copies (a weight section and the following — the same) of (a) ingredients, and it is 10-300 copies more preferably. Cohesive force becomes in the case of less than five copies, the toughness by an epoxy resin is not revealed, and insufficient for it. When exceeding 900 copies, the polymer which has a reactive silicon group which is the (a) ingredient is not incorporated into the matrix of a hardened material, but elasticity runs short, a hardened material becomes weak, and it is not desirable.

[0025]The silane coupling agent of the (c) ingredient contained in this invention, It is functional group content Silang which generally contain a hydrolytic silicon group and other functional groups in one molecule, and an amino group of the first class, the second class, and the third class, a sulfhydryl group, an epoxy group, an ureido group, an isocyanate group, a vinyl group, an methacrylic group, a halogeno alkyl group, etc. are mentioned as such a functional group. What has in this an amino group of the first class in which a reaction is possible, the second class, and the third class, a sulfhydryl group, an epoxy group, and an ureido group to the both sides of the polymer which has a reactive silicon group of the (a) ingredient, and the epoxy resin of the (b) ingredient is preferred. What has an amino group of an amino group especially the first class, and the second class is preferred more preferably. Although that whose X is a hydrolytic basis is used in the above-mentioned general formula and ** 1 as a hydrolytic silicon group and being got, the ease of handling, etc. to alkoxy silyl groups is preferred. As an example of these silane coupling agents, gamma-aminopropyl trimethoxysilane, gamma-aminopropyl triethoxysilane, gamma-aminopropyl methyl dimethoxysilane, gamma-aminopropyl methyldiethoxysilane, gamma-(2-aminoethyl) aminopropyl trimethoxysilane, gamma-(2-aminoethyl) aminopropyl triethoxysilane, gamma-(2-aminoethyl) aminopropyl methyl dimethoxysilane, gamma-(2-aminoethyl) aminopropyl methyldiethoxysilane, gamma-(5-aminopentyl) aminopropyl trimethoxysilane, gamma-(5-aminopentyl) aminopropyl triethoxysilane, gamma-(5-aminopentyl) aminopropyl methyl dimethoxysilane, gamma-(5-aminopentyl) aminopropyl methyldiethoxysilane, N-beta-(N-vinylbenzyl aminoethyl)-gamma-aminopropyl trimethoxysilane, Amino group content Silang, such as gamma-anilino propyltrimethoxysilane; gamma-mercapto propyltrimethoxysilane, gamma-mercaptopropyl triethoxysilane, gamma-mercaptpropylmethyl dimethoxysilane, Sulfhydryl group content Silang, such as gamma-mercapto propylmethyl diethoxysilane; Gamma-glycidoxypropyltrimetoxysilane, gamma-glycidoxy propyltriethoxysilane, gamma-glycidoxy propyl methyldimethoxysilane, Gamma-glycidoxypropylmethyldietoxysilane, beta-(3, 4-epoxycyclohexyl) ethyltrimethoxysilane, beta-(3, 4-epoxycyclohexyl) ethyltriethoxysilane, beta-(3,4-epoxycyclohexyl) ethyl methyl dimethoxysilane, Epoxy group content Silang, such as beta-(3,4-epoxycyclohexyl) ethyl methyldiethoxysilane; gamma-ureido propyltrimethoxysilane, Silane compounds, such as ureido group content Silang, such as gamma-ureido propyl triethoxysilane, gamma-ureido propylmethyl dimethoxysilane, and gamma-ureido propylmethyl diethoxysilane, are raised. These silane coupling agents may be used alone and may be used together two or more sorts.

[0026](c) As for an addition of an ingredient, 0.01-50 copies are preferred to 100 copies of (a) ingredients. Out of this range, control of effective phase structure cannot be performed, and when it is especially 0.01 or less copy, surface adhesiveness runs short and it is not desirable. They are 0.1-5 copies more preferably.

[0027]As a silanol condensation catalyst of the (d) ingredient contained in this invention, Titanate, such as tetrabuthyl titanate and tetrapropyl titanate; Dibutyltin dilaurate, Dibutyltin maleate, dibutyltin diacetate, octylic acid tin, Naphthenic acid tin, a reactant of dibutyltin oxide and phthalic ester, Organotin compounds, such as dibutyltin diacetyl acetonato; Aluminum tris acetylacetonato, Organoaluminium compounds, such as aluminumtrisethylacetoacetate and diisopropoxy aluminum ethylacetoacetate; Zirconium tetra acetylacetonato, chelate compound [, such as titanium tetra acetylacetonato,]; — organic-lead-

compounds [, such as lead octylate]; — a butylamine. Octylamine, lauryl amine, dibutyl amine, monoethanolamine, Diethanolamine, triethanolamine, diethylenetriamine, Triethylenetetramine, oleylamine, cyclohexylamine, benzylamine, diethylamino propylamine, xylylene diamine, a triethylene diamine, guanidine, diphenylguanidine, 2,4,6-tris(dimethyl aminomethyl) phenol, morpholine, Amine compounds, such as N-methyl-morpholine, 2-ethyl-4-methylimidazole, 1, and 8-diazabicyclo [5.4.0] undecene 7 (DBU), or salt [with carboxylic acid of these amine compounds, etc.]; — low-molecular-weight-polyamide resin; obtained from superfluous polyamine and polybasic acid, although a resultant of superfluous polyamine and an epoxy compound, etc. are illustrated, Not a thing limited to these but a condensation catalyst currently generally used can be used. These silanol condensation catalysts may be used alone and may be used together two or more sorts. A concomitant use system of organic metallic compounds or organic metallic compounds, and an amine compound is preferred from a point of hardenability among these silanol condensation catalysts. Especially, a tetravalent organotin compound is preferred also in organotin compounds, and when a tetravalent organotin compound and a compound which has an amino group of an amino group especially the first class, and the second class and a hydrolytic silicon group as a (c) ingredient are used together, it becomes what was excellent in especially an elastic modulus and intensity of a hardened material.

[0028](d) As for the addition of an ingredient, 0.01-20 copies are preferred to 100 copies of (a) ingredients, and it is 0.5-10 copies more preferably. When the crosslinking reaction of the polymer which has a reactive silicon group which is the (a) ingredient in the case of less than 0.01 copy becomes insufficient and it exceeds 20 copies, it is possible to have an adverse effect on an adhesive property etc., and is not desirable.

[0029]As an epoxy resin hardener of the (e) ingredient contained in this invention, Triethylenetetramine, tetraethylenepentamine, diethylamino propylamine, N-aminoethyl piperazine, MENSENJI amine, isophoronediamine, Morpholine, piperidine, m-xylylene diamine, m-phenylenediamine, The first classes, such as diaminodiphenylmethane and diaminodiphenyl sulfone, The second class amines; Trialkylamine, N-methyl-morpholine, N, and N'-dimethylpiperazine, Pyridine, picoline, guanidine, diphenylguanidine, 1, 8-diazabicyclo [5.4.0] undecene 7 (DBU), Benzyldimethylamine, 2-(dimethyl aminomethyl) phenol, The third class amines, such as 2,4,6-tris(dimethyl aminomethyl) phenol, And the organic acid salt; 2-methylimidazole, 2-ethyl-4-methylimidazole, Imidazole-derivatives; polyamide resin; dicyandiamide; boron trifluoride-amine complexes, such as 2-undecylimidazole and 1-benzyl-2-methylimidazole; Phthalic anhydride, hexahydro phthalic anhydride, tetrahydro phthalic anhydride, And methylene tetrahydro phthalic anhydride, a dodecylsuccinic anhydride, Anhydrous carboxylic acid; alcohols; phenols; carboxylic acid, such as trimellitic anhydride, pyromellitic dianhydride, and anhydrous KUROREN acid; Boron trifluoride, Although Lewes acids, such as phosphorus hexafluoride, trichloride aluminum, and a tin tetrachloride, the salts of those, etc. are illustrated, it is not limited to these, and the epoxy resin hardener currently generally used can be used. These epoxy resin hardeners may be used alone and may be used together two or more sorts. The third class amines and its organic acid salt, and imidazole derivatives are preferred from a point of hardenability among these epoxy resin hardeners.

[0030](e) What is necessary is just to use it according to the purpose to 100 copies of (b) ingredients in 0.01-300 copies, although an addition of an ingredient changes with the kind and kinds of epoxy resin of the (b) ingredient.

[0031](a) There is no limitation in particular in the method of preparation of a hardenability resin composite containing an ingredient, the (b) ingredient, the (c) ingredient, the (d) ingredient, and the (e) ingredient, For example, the (a) ingredient, the (b) ingredient, the (c) ingredient, the (d) ingredient, and the (e) ingredient are blended, it mulls using a mixer, a roll, or a kneader, or each ingredient is dissolved using a suitable solvent, a usual method of mixing is adopted, and it gets. It is also possible by combining each ingredient suitably to build and use 1 liquid type and a two-component compound.

[0032]In a constituent of this invention, further if needed A dehydrator, a compatibilizer, an adhesive improving agent, Various additive agents, such as a physical-properties regulator, a preservation stability improving agent, a bulking agent, an antiaging agent, an ultraviolet ray absorbent, a metal deactivator, anti-ozonant, light stabilizer, amine system radical chain inhibitor, a phosphorus system peroxide decomposition agent, lubricant, paints, and a foaming agent, can be added suitably.

[0033]When using a bulking agent as an additive agent, for example, wood flour, walnut shell powder, chaff powder, Pulp, a cotton chip, mica, graphite, diatomite, clay, kaolin, Asbestos, glass fiber, carbon fiber, etc. are used and it gets in a glass bead, calcium carbonate, magnesium carbonate, titanium oxide, an aluminium powder, and the end of zinc dust in clay, talc, fumed silica, sedimentation nature silica, a silicic acid anhydride, and the end of quartz powder. These bulking agents may be used independently and may be used together two or more sorts.

[0034]Other polymers which have a reactive silicon group other than a polymer of the (a) ingredient, for example, reactive silicon group content polypropylene oxide, other reactive silicon group content polyether, a polydimethyl siloxane, etc. may be added.

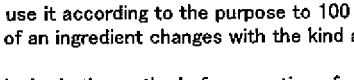
[0035]A hardenability resin composite of this invention is excellent in an adhesive property. A hardened material of a rate of high elasticity which raised cohesive force of not only a hardened material of high elongation but a matrix with a low elastic modulus, and high tension shear strength can be obtained by changing an addition of a silane coupling agent. Therefore, it can use to the dynamic characteristic demanded as adhesives which can respond, a sealing compound, and a binder by an easy means referred to as changing an addition of a silane coupling agent.

[0036]

[Working example]This invention is explained still more concretely based on an embodiment.

300 g of polytetramethylene glycols of the example of manufacture 1 hydroxyl value 27.3 and the average molecular weight 4,110 are put into 1-l. autoclave, After adding 46.5 g of CH_3ONa28% methanol solution and carrying out decompression degassing at 130 ** for about 6 hours, a 24-ml allyl chloride was dropped and was made to react for about 2 hours. It was checked that allyl ether groups are introduced into 80% of whole ends by iodine value measurement. After putting 200 g of this allyl ether end polytetramethylene oxide into a 500-ml 4 mouth flask, 100microl Adding the 10% ethanol solution of chloroplatinic acid and dropping methyl dimethoxysilane at 50 **, it was made to react at 80 ** for about 3 hours. ^1H-NMR measurement [0037]

[Chemical formula 4]



$$(CH_3O)_2SiCH_2CH_2CH_2O-$$

It was checked that polytetramethylene oxide of the average molecular weight 4,400 [about] which has 1.6 structures per molecule had been obtained.

Using the tetrahydrofuran propylene oxide random copolymer of the example of manufacture 2 hydroxyl value 28.0, the average molecular weight 4,007, and 10 weight % of propylene oxide contents, by the same method as the example 1 of manufacture. The tetrahydrofuran propylene oxide random copolymer of the average molecular weight 4,300 [about] which has 1.6 structures per molecule expressed with an end by the above-ization 4 was obtained.

The average molecular weight which introduced the example of manufacture 3 allyl ether end into 90% of whole ends uses the tetrahydrofuran propylene oxide random copolymer whose propylene oxide content is 10 weight % in 6,600, The tetrahydrofuran propylene oxide random copolymer of the average molecular weight 6,800 [about] which has 1.4 structures per molecule which hydrosilylate by the same method as the example 1 of manufacture, and are expressed with an end by the above-ization 4 was obtained.

An average molecular weight which introduced an example of manufacture 4 allyl ether end into 90% of whole ends uses a tetrahydrofuran propylene oxide random copolymer whose propylene oxide content is 10 weight % in 8,200, A tetrahydrofuran propylene oxide random copolymer of the average molecular weight 8,400 [about] which has 1.6 structures per molecule which hydrosilylate by the same method as the example 1 of manufacture, and are expressed with an end by the above-ization 4 was obtained.

A polytetramethylene **********-**** propylene oxide polytetramethylene oxide triblock copolymer of the example of manufacture 5 hydroxyl value 28.7, the average molecular weight 3,910, and 50 weight % of propylene oxide contents is used, A polytetramethylene **********-**** propylene oxide polytetramethylene oxide triblock copolymer of the average molecular weight 4,100 [about] which has 1.6 structures per molecule expressed with an end by the above-ization 4 by the same method as the example 1 of manufacture was obtained.

Polypropylene oxide of the average molecular weight 5,000 which introduced an example of manufacture 6 allyl ether end into 97% of whole ends is used, Polypropylene oxide of the average molecular weight 5,200 [about] which has 1.7 structures per molecule which hydrosilylate by the same method as the example 1 of manufacture, and are expressed with an end by the above-ization 4 was obtained.

Polytetramethylene oxide of the average molecular weight 4,400 which has the reactive silicon group obtained in Embodiments 1-8, the comparative example 1 - the example 1 of 2 manufactures, epoxy resin Epicoat #828 (oil recovery shell epoxy company make and an epichlorohydrin bisphenol A type epoxy resin.) the weight per epoxy equivalent about 190 silane coupling agent A1122 (Nippon Unicar make.) gamma-(2-aminoethyl) aminopropyl trimethoxysilane and silanol condensation catalyst #918 (the Sankyo Organic

Chemicals make.) 1:1 mixture [of dibutyltin oxide and dioctyl phthalate] and epoxy resin curing catalyst DMP30 (the Kayaku Nooly Co., Ltd. make, 2,4,6-tris(dimethyl aminomethyl) phenol) was mixed by presentation (weight section) shown in Table 1, and a hardenability resin composite was obtained.

[0038]

[Table 1]

		比較例	実施例											比較例			
		1	1	2	3	4	5	6	7	8	9	10	11	12	3	4	5
反応性ケイ素基を有する重合体	製造例1	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
	製造例2	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	製造例3	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	製造例4	—	—	—	—	—	—	—	—	—	—	—	100	—	—	—	—
	製造例5	—	—	—	—	—	—	—	—	—	—	—	—	100	—	—	—
	製造例6	—	—	—	—	—	—	—	—	—	—	—	—	—	100	100	100
エポキシ樹脂 #828		50	50	50	50	50	100	100	100	100	50	50	50	50	50	50	50
シランカップリング剤 A1122		—	1	2	5	7.5	—	1	2	5	7.5	2	2	2	—	1	2
シラノール縮合触媒 #918		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
エポキシ樹脂硬化触媒 DMP30		5	5	5	5	5	10	10	10	10	5	5	5	5	5	5	5

A tetrahydrofuran propylene oxide random copolymer of the average molecular weight 4,300 [about] which has the reactive silicon group obtained in the example 2 of embodiment 9 manufacture 100 copies, 50 copies and the silane coupling agent A1122 were carried out for epoxy resin Epicoat #828, one copy and five copies of epoxy resin curing catalyst DMP30 were mixed for two copies and silanol condensation

catalyst #918 like Embodiment 2, and a hardenability resin composite was obtained.

The hardenability resin composite was obtained like Embodiment 9 except having used the tetrahydrofuran propylene oxide random copolymer of the average molecular weight 6,800 [about] which has the reactive silicon group obtained in the example 3 of embodiment 10 manufacture.

The hardenability resin composite was obtained like Embodiment 9 except having used the tetrahydrofuran propylene oxide random copolymer of the average molecular weight 8,400 [about] which has the reactive silicon group obtained in the example 4 of embodiment 11 manufacture.

The hardenability resin composite was obtained like Embodiment 9 except having used the polytetramethylene **********-**** propylene oxide polytetramethylene oxide triblock copolymer of the average molecular weight 4,100 [about] which has the reactive silicon group obtained in the example 5 of embodiment 12 manufacture.

Polypropylene oxide of the average molecular weight 5,200 which has the reactive silicon group obtained in the comparative example 3 - the example 6 of 5 manufactures, Epoxy resin Epicoat #828, silane coupling agent A1122, and silanol condensation catalyst #918 and epoxy resin curing catalyst DMP30 were mixed by the presentation (weight section) shown in Table 1, and the hardenability resin composite was obtained.

[0039]The following examinations estimated the above-mentioned hardenability resin composite.

1) The dumbbell tensile test above-mentioned hardenability resin composite was slushed into the mold made from Teflon, it was recuperated at 50 ** at 23 ** on the 4th on the 3rd, and the sheet-shaped hardened material was obtained. Based on JIS K6301, the No. 3 type dumbbell is pierced from this sheet-shaped hardened material, At the time of 30% tension, at the time of 50% tension, it was extended at the time of each modulus at the time of 100% tension (M_{30}, M_{50}, M_{100}), breaking strength (TB), and a fracture, and (EB) was measured by speed-of-testing 200 mm/min.

2) Measurement based on tensile shear strength measurement JIS K 6850 was performed. The surface of the aluminum plate (100mmx25mmx2mm A-1050P aluminum plate specified to JISH 4000) was lightly wiped with acetone, and the above-mentioned hardenability resin composite was applied to the range of a size (about 25 mm x 12.5 mm) at about 0.05 mm in thickness with the spatula. Then, the spreading sides of the aluminum plate with which the above-mentioned hardenability resin composite was applied were pasted together, and it was stuck by pressure by hand. The adhesion side of this specimen was fixed and it was recuperated at 50 ** at 23 ** on the 4th on the 3rd. Then, it asked for the tensile shear strength by breaking the value obtained by measuring maximum load until the hardened material portion of a specimen is destroyed by speed-of-testing 5 mm/min by a coated area.

[0040]The result of the above-mentioned examination and measurement was shown in Table 2 and Table 3.

[0041]

[Table 2]

	シランカップリング剤の添加量（重量部）	ダンベル引張物性 M_{30} M_{50} M_{100} (kgf/cm²)	T B (kgf/cm²)	E B (%)	せん断強度 (kgf/cm²)
比較例1	0	3.5 4.6 8.1	107	515	61.9
実施例1	1	10.4 15.9 31.6	81.9	224	98.7
実施例2	2	21.9 32.7 59.6	90.5	158	147
実施例3	5				142
実施例4	7.5				143
比較例2	0	10.4 16.0 32.3	128	310	51.7
実施例5	1	34.6 50.2 -	67.5	71	115
実施例6	2	86.9 114 -	116	51	165
実施例7	5				128
実施例8	7.5				116
比較例3	0	3.3 5.4	27.4	460	21.1
比較例4	1	7.1 13.6	62.5	290	93.8
比較例5	2	10.7 21.2	68.2	250	100

[0042]
[Table 3]

	使用重合体	ダンベル引張物性 M_{50} M_{100} (kgf/cm²)	T B (kgf/cm²)	E B (%)	せん断強度 (kgf/cm²)
実施例2	製造例1	32.7 59.6	90.5	158	147
実施例9	製造例2	36.9 64.4	77.7	125	180
実施例10	製造例3	27.4 46.3	74.4	180	100
実施例11	製造例4	24.9 41.8	112	314	143
実施例12	製造例5	37.9 67.1	121	189	92
比較例5	製造例6	10.7 21.2	68.2	250	100

3) After it used as the frozen ultra thin section the hardened material obtained by the transmission electron microscope observation above-mentioned examination 1 and osmic acid dyed it, transmission electron microscope observation was performed with the accelerating voltage of 200 kV using the transmission electron microscope (the JEOL Co., Ltd. make, JEM-2000FX).
[0043]The comparative example 1 was shown in Embodiment 9 and drawing 3, and the transmission electron microscope observation photograph of the comparative example 4 was shown in drawing 1 at drawing 4 at Embodiment 2 and drawing 2.

[0044]While the tensile shear strength is higher than it can set to a comparative example in the embodiment of this invention so that more clearly than Table 2, the modulus of the hardened material changes a lot with the increase in the addition of a silane coupling agent.
[0045]The hardened material of the constituent using the various polymers of the (a) ingredient contained in this invention is a high modulus from it of a comparative example so that more clearly than Table 3. High cohesive force is shown.

[0046]In the transmission electron microscope observation images of Embodiment 2 shown in drawing 1, Compared with the thing of the comparative example 1 shown in drawing 3, the particle diameter of the particle state domain considered to be the hardened epoxy resin which is dyed with osmic acid becomes small, And it is suggested that the volume ratio of a domain and a matrix is smaller than the composition ratio (50/100) of the epoxy resin and reactive silicon group content polymer in a constituent, and there are many amounts of epoxy resins in a matrix. It is possible that it originates in these things and the hardened material of an embodiment serves as a high modulus. It is clear by comparing drawing 1 (embodiment 2) and drawing 2 (embodiment 9) with the transmission electron microscope observation images of drawing 4 (comparative example 4) this' to be observed by the thing using the various polymers of the (a) ingredient contained in this invention.
[0047]
[Effect of the Invention]According to this invention, the hardenability resin composite excellent in the adhesive property is provided. The hardened material of the rate of high elasticity which raised the cohesive force of not only the hardened material of high elongation but the matrix with the low elastic modulus, and high tension shear strength can be obtained by controlling the addition of a silane coupling agent.
[0048]The hardenability resin composite of this invention can be used to the dynamic characteristic demanded as the adhesives which can respond, a sealant, and a binder by the easy means referred to as changing the addition of a silane coupling agent.

[Translation done.]

* NOTICES *

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1]It is a transmission electron microscope observation photograph which shows the phase structure of the hardened material obtained from the constituent of Embodiment 2 of this invention.
[Drawing 2]It is a transmission electron microscope observation photograph which shows the phase structure of the hardened material obtained from the constituent of Embodiment 9 of this invention.
[Drawing 3]It is a transmission electron microscope observation photograph which shows the phase structure of the hardened material obtained from the constituent of the comparative example 1.
[Drawing 4]It is a transmission electron microscope observation photograph which shows the phase structure of the hardened material obtained from the constituent of the comparative example 4.

[Translation done.]

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最終頁に続く

(54)【発明の名称】　硬化性樹脂組成物

1

(57)【特許請求の範囲】

【請求項１】（ａ）反応性ケイ素基を有し、実質的な繰り返し単位が

$-CH_2\ CH_2\ CH_2\ CH_2\ O-$

である重合体、

（ｂ）ビスフェノールＡ型エポキシ樹脂、

（ｃ）１分子中にアミノ基とアルコキシシリル基を含有するシランカップリング剤、

（ｄ）４価のスズを含有するスズ化合物であるシラノール縮合触媒、及び

（ｅ）三級アミン化合物またはその塩であるエポキシ樹脂硬化剤

よりなる硬化性樹脂組成物。

【請求項２】（ａ）成分の重合体の主鎖が、テトラヒドロフランから開環重合により得られるポリエーテル、あ

2

るいはテトラヒドロフランと環状エーテルとから開環重合により得られるポリエーテルであることを特徴とする請求項１記載の硬化性樹脂組成物。

【請求項３】（ｂ）成分が、ビスフェノールＡとエピクロルヒドリンより得られるエピクロルヒドリン－ビスフェノールＡ型エポキシ樹脂であることを特徴とする請求項１又は２記載の硬化性樹脂組成物。

【請求項４】（ｃ）成分のシランカップリング剤の配合割合が、（ａ）成分１００重量部に対して０．０１～５０重量部であることを特徴とする請求項１～３のいずれか１項に記載の硬化性樹脂組成物。

【請求項５】（ｄ）成分のシラノール縮合触媒の配合割合が、（ａ）成分１００重量部に対して０．０１～２０重量部であることを特徴とする請求項１～４のいずれか１項に記載の硬化性樹脂組成物。